

UNIT 1

CHEMICAL ENERGETICS: BASIC ASPECTS

Structure

1.1	Introduction	1.4	Work, Heat and Heat Capacity
	Expected Learning Outcomes	1.5	Reversible and Irreversible Processes
1.2	Chemical Thermodynamics and its Importance	1.6	Thermal Equilibrium: The Zeroth Law of Thermodynamics
1.3	Thermodynamic Terminology	1.7	Summary
	Thermodynamic System	1.8	Terminal Questions
	State of a System	1.9	Answers
	Extensive and Intensive Variables		
	Thermodynamic Processes		

1.1 INTRODUCTION

'Energetics' refers to the study of energy in terms of its flow and transformation within a system or between a system and its surroundings. The energy could be in the form of heat, radiation, work or some other means. Energetics is very broad field and its applicability in a given area can be qualified by putting a suitable prefix before it. For example, the term chemical energetics implies the study of flow and transformation of energy in chemical systems. Similarly, the term bioenergetics refers to the study of flow and transformation of energy in biological systems and so on so forth. In this course we are going to focus our attention on the flow and transformation of energy within chemical systems or between the chemical systems and their surroundings.

We would begin the unit by defining thermodynamics and outlining its significance in Chemistry. It would be followed by definition and explanation of the terminology needed to understand and appreciate different aspects of thermodynamics. Many of these terms may sound quite familiar to you; however, we would be defining them precisely in the context of thermodynamics. Having defined these, we would revisit the concepts of heat, work and heat capacity. We would then explain the meaning of thermodynamic

reversibility followed by the concept of thermal equilibrium. The understanding of thermal equilibrium would then be used to formulate the Zeroth law of thermodynamics.

In the next unit we would take up the First law of thermodynamics.

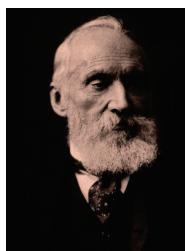
Expected Learning Outcomes

After studying this unit, you should be able to:

- ❖ define energetics;
- ❖ define chemical thermodynamics and outline its significance;
- ❖ explain different types of thermodynamic systems;
- ❖ explain the meaning of thermodynamic state of a system;
- ❖ define and differentiate between intensive and extensive variables giving examples;
- ❖ define different types of thermodynamic processes;
- ❖ explain the meaning of work and heat and discuss about their interconvertibility;
- ❖ define heat capacity, discuss its different types and state relationship between them;
- ❖ explain the concept of thermodynamic reversibility with the help of suitable examples;
- ❖ differentiate between thermodynamic reversibility and irreversibility;
- ❖ define thermal equilibrium and outline the requirements to achieve the same; and
- ❖ state and explain the Zeroth law of thermodynamics.

Thermodynamics is the only physical theory of a general nature of which I am convinced that it will never be overthrown.

— Albert Einstein



Lord Kelvin
(William Thomson)

1.2 CHEMICAL THERMODYNAMICS AND ITS IMPORTANCE

Thermodynamics is an experimental science based on certain generalisations formulated on the basis of extensive observations of the macroscopic world. Macroscopic means something that can be felt, seen or handled e.g., things that can be seen by naked eyes. These generalisations are termed as the laws of thermodynamics and are applicable to all macroscopic systems, irrespective of their physical state- solid, liquid, gas, or any combination of these states. The term thermodynamics was coined by Lord Kelvin (1824-1907) to signify the dynamic nature of heat, which was then considered to be a kind of fluid. The term is based on two Greek roots, viz., 'thermo' meaning heat or temperature and 'dunamikos' meaning movement. If we take literal translation, thermodynamics means dynamics (or motion) of heat. We would be talking about the laws of thermodynamics and their significance in this course.

Importance of Thermodynamics

It is important to note that the thermodynamics is concerned only with macroscopic or large-scale properties of matter and make no assumptions about the microscopic structure of matter i.e., the structure of atom or molecules. It implies that the laws of thermodynamics are independent of the structure of atom, which in turn means that *even if the structure of atom as we know today, is modified; the laws of thermodynamics and their applicability will not change*. In fact, the laws of thermodynamics were formulated mainly in the nineteenth century well before the classical and quantum mechanical description of the structure of atom was understood. It is worthwhile to mention that there has not been even a single example that violates these laws.

Another important aspect of the thermodynamics is that it is an exact science and its laws can be expressed in terms of mathematical relationships. This allows us to derive mathematical equations that can describe and predict the outcome of many chemical and physical processes. This in turn allows us to apply these laws to practically all the branches of Science and Engineering.

In the context of chemical systems, the primary objective of thermodynamics is to establish a criterion for determining the feasibility (or spontaneity) of a given physical or chemical transformation. Secondly, thermodynamics can help in determining the criteria and conditions for the equilibrium state for a spontaneous process. The thermodynamic data can also be used to predict the direction in which the system would move to attain equilibrium and also provide the information about the extent of reaction for a given chemical reaction.

It's time that we take up the terminology used in thermodynamics. You should pay attention to the terms being discussed, as you would be using them extensively in the course of your learning thermodynamics. It is, therefore, essential that you have proper understanding of these terms. Answer the following simple question before moving ahead.

SAQ 1

What is the importance of thermodynamics in the context of chemical reactions?

Thermodynamics, like classical mechanics and classical electromagnetism, is an exact mathematical science. Each such science may be based on a small finite number of premises or laws from which all the remaining laws of the sciences are deductible by purely logical reasoning.

— Guggenheim

1.3 THERMODYNAMIC TERMINOLOGY

A number of terms are used in the study of thermodynamics and these have specific meaning. Let us learn about some of the commonly used terms in the field of thermodynamics. Some of these may appear to be obvious or trivial but we need to define and understand them so that there is no ambiguity in their usage.

1.3.1 Thermodynamic System

A 'system' in thermodynamics is defined as *that part of the universe, which is under consideration for the study*. The system can be large or small; simple or complex. For example, a system could just be as small and simple as a beaker containing certain volume of distilled water or as large and complex as the ocean, Fig 1.1.



(a)

(b)

Fig. 1.1: A thermodynamic system can be of any size: (a) a beaker containing certain volume of distilled water (b) an ocean.

A thermodynamic system must have well defined boundaries that may be real (fixed or moveable) or imaginary. A capped glass vial containing water or a reaction mixture; Fig.1.2 (a) has defined physical boundaries whereas the ozone hole in the stratosphere layer of the earth's atmosphere; Fig.1.2 (b) does not have real boundary but it is also a thermodynamic system. Further, the boundaries of the system could be either fixed e.g., a fixed volume cylinder; Fig.1.2 (c) or movable e.g., a cylinder fitted with movable piston Fig. 1.2 (d).

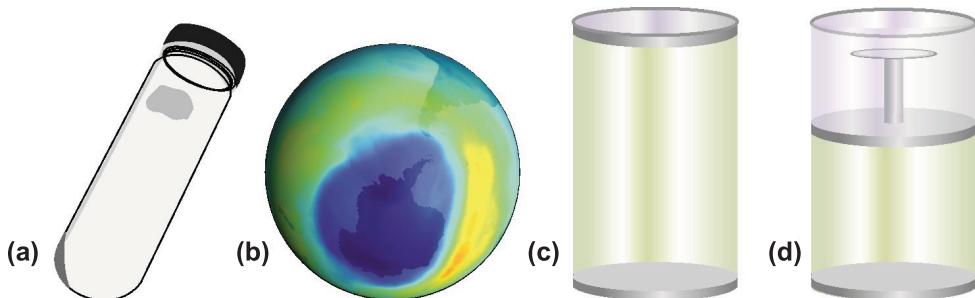
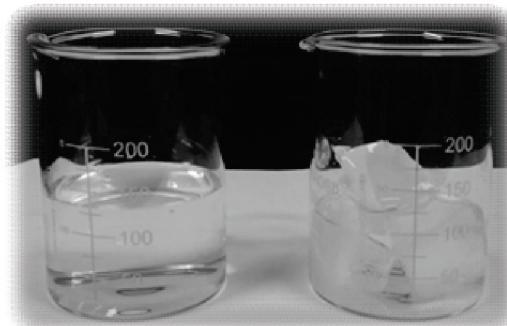


Fig. 1.2: The boundaries of a thermodynamic system can be: (a) real, (b) imaginary, (c) fixed, or (d) movable.

In addition, the system may be homogenous or heterogeneous; Fig.1.3 (a). A **homogeneous system** is the one whose properties are uniform throughout the system. A beaker containing an aqueous solution of salt or sugar in water is a common example of homogenous systems. On the other hand, a **heterogeneous system** consists of two or more homogeneous systems that are separated by physical boundaries. A beaker containing ice in water is a common example of heterogeneous systems; Fig.1.3 (b).



(a)

(b)

Fig. 1.3: The thermodynamic system can be: (a) homogeneous (salt in water) or (b) heterogeneous (ice in water).

Surroundings

Theoretically speaking, the remaining (other than the *system*) part of the universe constitutes the **surroundings** of the system. The system and its surroundings put together constitute the **universe**. However, *practically speaking, the surroundings are that part of the universe with which the system can interact*. For the examples given above,

- i) The surroundings of the system of test tube containing distilled water, are its immediate surroundings—the laboratory bench, the people around or may be the laboratory as a whole.
- ii) Similarly, for the ozone hole as the system, the surroundings may include the adjoining part of the stratosphere, the lower part of the mesosphere (the layer above the stratosphere) and the upper portions of the troposphere (the layer below the stratosphere).

Types of Systems

A system is always separated from its surroundings by a **boundary**. The type of thermodynamic system depends on the characteristics of the boundary. If the boundary of the system is such that it allows the transfer of matter and energy between the system and its surroundings through it, the system is classified as an **open system**. A glass test tube containing hot water is an example of an open system as water can be removed or more water or some other kind of matter can be added to it and also the temperature of water can be increased (by heating it) or decreased (by allowing it to cool down) by suitable transfer of energy.

The system, whose boundary does not permit the transfer of matter between the system and its surroundings but allows transfer of energy, is called a **closed system**. If the glass test tube containing hot water is suitably capped such that the matter exchange is not allowed, it would become a closed system. You may note here that the energy exchange can still happen and the temperature of water in the tube can be increased or decreased.

A closed system having a boundary that does not permit the transfer of heat to or from the surroundings is termed as an **isolated system**. In this case neither the matter nor the energy can be exchanged with the surroundings.

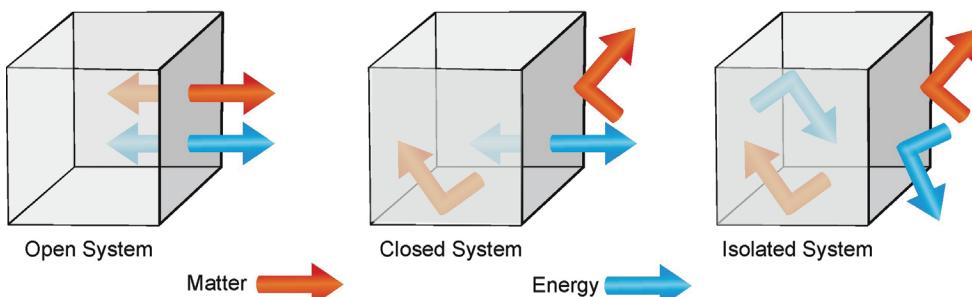


Fig. 1.4: Types of thermodynamic systems: in open system, both energy and matter can be exchanged with surroundings; closed system allows exchange of energy only whereas the isolated system does not allow exchange of either matter or energy.

If the suitably capped glass test tube containing hot water is placed inside a thermos flask or is wrapped with a thick thermally insulating material, it would become an isolated system, as then neither the matter nor energy exchange would be possible between the system and its surroundings. Different types of thermodynamic systems are schematically shown in Fig. 1.4.

Hope you have understood the types of thermodynamic systems, attempt the following simple question to assess your understanding of the types of systems.

SAQ 2

Differentiate between open, closed and isolated systems with the help of suitable examples. (Provide your own examples; do not use examples given above).

1.3.2 State of a System

The pressure, P ; volume, V ; temperature, T ; and density, ρ , are examples of some of the thermodynamic properties or thermodynamic variables of a system. These are used interchangeably.

We have so far defined a thermodynamic system and its types. Let us raise a question, "How do we characterise or describe a thermodynamic system?" It is obvious that different systems say water in a test tube or the ozone hole would have different descriptions. One of the ways of characterising or defining a thermodynamic system is in terms of its measurable physical properties like pressure, temperature and volume etc. That is if we specify the physical properties of the system, we say that we have defined the state of the system. These properties are called **thermodynamic properties** or variables. The thermodynamic variables are also called **state variables** as these depend on the given state of the system and not on the past history of the system.

If we know the values of the thermodynamic properties of the system we say that the state of a system is defined or known.

Further, a state variable which depends on other variables is called a **dependent variable** and the variables on which it is dependent, are called **independent variables**. For example, if we have a sample of ideal gas taken in a cylinder fitted with a piston. Then according to the ideal gas equation, viz., $pV = nRT$, we can write $V = nRT/p$ i.e., the volume of the gas depends on the amount, n ; temperature, T and pressure, p . Here, the volume is the dependent variable whereas the amount of gas, pressure and temperature are independent variables. On the other hand, if we wish to talk about the pressure of the gas in terms of other variables, then the pressure becomes dependent while n , T and V become independent variables. In other words, we can say that the choice of dependent and independent variables for a thermodynamic system is a matter of convenience.

1.3.3 Extensive and Intensive Variables

Thermodynamic variables of a given system can be divided into two groups' viz., intensive and extensive variables. An intensive variable is the one whose value is independent of the amount (mass) of the system whereas the extensive variables depend on the amount of the system. For example, temperature is an intensive variable; the temperature of a small chunk of ice broken from a slab of ice would be same as that of the slab. On the other hand volume is an extensive variable; the volume of 10 moles (1.8 kg) of glucose

would be more than that of 1.0 mole (180 g) of glucose. It is important to note that the ratio of any two extensive variables is an intensive variable. For example, density- a ratio of two extensive variables viz., mass and volume, is an intensive variable.

The ratio of an extensive variable to the mass of the system (i.e., property per unit mass) is called **specific property** and is intensive e.g., specific volume. Similarly, the ratio of an extensive variable to the number of moles of the substance in the system i.e., the property per mole is called **molar property** and is also intensive. Answer the following self assessment question to gauge your learning about the intensive and extensive variables.

All that is stated about intensive and extensive variables holds for a homogenous system. As regards the heterogeneous system consisting of number of phases, some of the intensive variables may be different for different phases.

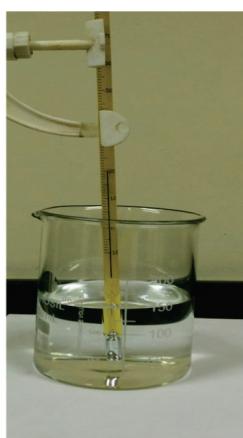
SAQ 3

Categorise the following properties into extensive and intensive properties:

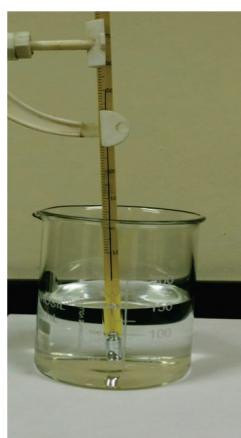
Volume, area, density, refractive index, temperature, dielectric constant, pressure, energy

1.3.4 Thermodynamic Processes

In our discussion so far you have learnt about thermodynamic systems, their types and the variables that characterise the state of a given system. When a thermodynamic system undergoes a change in its state we say a **thermodynamic process** has occurred. Suppose we take 150 g of distilled water at 20°C in a beaker and heat it so that the temperature becomes 50°C; we have performed a thermodynamic process. In the course of a thermodynamic process the system can undergo an exchange of matter and/or energy with the surroundings. A thermodynamic process or a change in state is defined by clearly specifying the *initial* and *final states* of the system. The initial and final states in this example would be characterised as (p , 150 g, 20°C) and (p , 150 g, 50°C) respectively; here p is the atmospheric pressure (as the beaker is uncovered); Fig. 1.5. It is assumed that there is no loss of water due to evaporation.



Initial state
(p , 150 g, 20°C)



Final state
(p , 150 g, 50°C)

Fig. 1.5: A thermodynamic process involves a change in at least one of the thermodynamic variables.

You may note here that in the process described here, only one thermodynamic parameter, viz.; the temperature has undergone a change whereas other parameters like volume and pressure have not changed significantly. Thus, *for a change of state or a thermodynamic process to occur, at least one of the thermodynamic variables must change*. Can you think of any process where none of the thermodynamic variables characterising the state of the system undergoes a change?

The answer is obvious, if none of the thermodynamic variables characterising the state of the system undergoes a change, the state of the system remains unchanged and it means that no process has occurred. However, sometimes it may so happen that the system undergoes a number of changes in state such that it comes back to its initial state with same characteristics. Such a process is referred to as a **cyclic process**.

Different types of thermodynamic processes are given below. Some of these thermodynamic processes occur in such a way that one of the variables does not change (remains invariant). These processes are given special names and are used very often.

You would learn about thermal equilibrium in Section 1.5

You would learn about bomb calorimeter in Unit 3

In addition to the thermodynamic processes given here, wherein some of the thermodynamic properties were allowed to change or remain constant we have two more types of processes which basically concern about the way the process is performed or allowed to occur. These are called reversible and irreversible processes. You would learn about these processes in Section 1.4

- i) **Isothermal Process:** (pronounced as “eye-so-therm-al”): As is obvious from the name it is a process in which the temperature of the system remains constant. For example, the conversion of 1 mole of ice into water at its melting point (273.16 K; 1 atm) is an example of an isothermal process. Isothermal processes are carried out in such a way that any heat flow into or out of the system occurs so slowly that the thermal equilibrium between the system and the surroundings is maintained.
- ii) **Adiabatic Process** (pronounced as “ay-dee-ah-bat-ic”): It is a process in which no energy as heat is allowed to enter or leave the system. Such a process occurs in systems that are thermally insulated and are accompanied by a change in the temperature of the system.

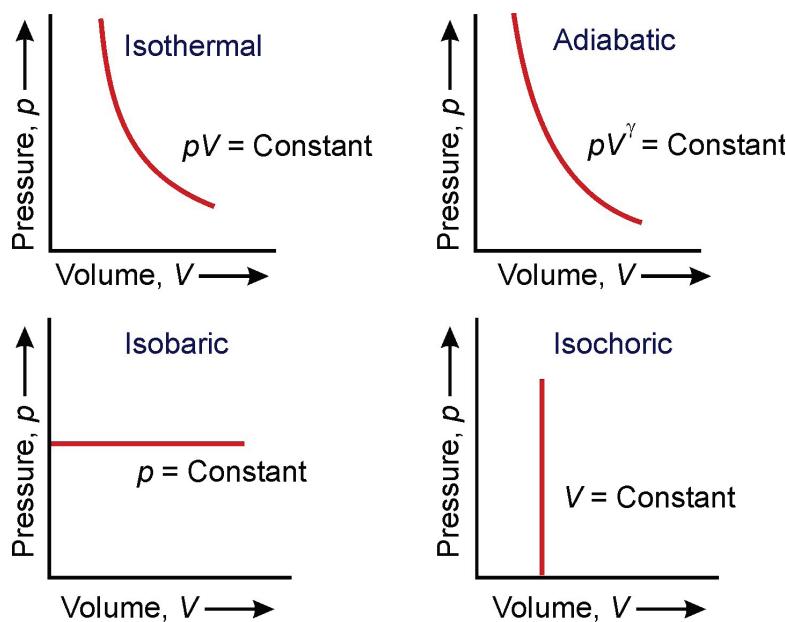


Fig. 1.6: Indicator diagrams showing the pV graphs for different types of thermodynamic processes for a gaseous system.

- iii) **Isobaric Process** (pronounced as “eye-so-bear-ic”) sometimes also called as isopiestic process: It is a process, which is accompanied by no change in the pressure of the system. Heating of water in an open vessel or expansion of a gas in a cylinder fitted with a massless and frictionless piston are the examples of isobaric processes. In both of these cases the pressure is equal to the atmospheric pressure.
- iv) **Isochoric Process** (pronounced as “eye-so-kor-ic”) sometimes also called as isovolumetric process: It is the process in which the volume of the system remains constant. Combustion of a substance in a bomb calorimeter about which you would learn in Unit 3, is an example of an isochoric process.

These processes for a gaseous system can be represented in terms of pV diagrams called **indicator diagrams**, Fig.1.6. In order to move on to the laws of thermodynamics, we need to recall a few important concepts viz., work, heat and heat capacity that you would have learnt in your earlier classes. It is essential to clearly understand the definitions of work and heat, and the distinction between the two so as to understand the exchange of energy between a thermodynamic system and its surroundings.

Solving the self-assessment question 4 would help you assess your understanding of thermodynamic state and processes.

SAQ 4

- a) What is meant by the state of a thermodynamic system?
- b) Can a cyclic process be a one step process? Comment.

1.4 WORK, HEAT AND HEAT CAPACITY

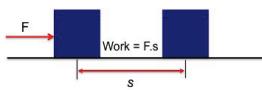
We all do work and know it as any activity that requires muscular or mental effort. The muscular effort typically involves pulling, pushing or lifting an object. In each of these, when we exert a force on a body such that the body moves from one place to another i.e., gets displaced; we say work has been done. Greater the displacement more the work, *if however, there is no displacement there is no work*. For example, suppose you start pushing a wall there is no work irrespective of the force applied by you, as the wall does not move. These examples on mechanical work can be used to give a definition for work.

Let us see the consequence of applying force in the examples given above. We find that the application of force causes an increase in the kinetic energy of the objects. Thus, there is transfer of some kind of energy from the person to the object. This transfer of energy is called **work**. Therefore, we may define work to be *transfer of energy via force*. You may see in the figure given in the margin that a force F is applied on the block and it moves by a distance s . In this case there has been a transfer of energy from the person to the object (block) we say the work has been done on the block. Mathematically, the work can be given as the product of the magnitude of force F applied and the magnitude of displacements:



$$w = F.s$$

...(1.1)



Note:

We should keep in mind that work is **NOT** a material /substance that is physically transferred from the person to the object or vice-versa.

Here again, as in case of work, you have to keep in mind that heat also is **NOT** a substance or material. It is just energy in transit. There is nothing as 'the amount of heat in a body'

Though, historically the heat was thought to be a substance and was called 'caloric'. Around 1780 Benjamin Thompson (Count Rumford) demonstrated using boring of cannon barrels that the amount of heat was related to the amount of work done in the process. This was later, shown by Joule in 1840s that heat like work was energy and the two were interconvertible.

There can be transfer of energy from the object also. Suppose an object is in motion and a person slows it down by applying force in a direction opposite to its motion. In such a case the kinetic energy of the object would decrease and an equivalent amount of energy will be transferred from the object to the person. We say that, the object has done work on the person. Such a work is called the negative work. Thus, we may define **work** as,

"The energy transferred to or from an object by means of a force acting on the object. The work is said to be positive if the energy is transferred to the object (its energy increases), and negative if the energy is transferred from the object (its energy decreases)"

However, in thermodynamics we get more specific and define work as,

"A quantity of energy that flows across the boundary of a system by means of a force during a change in its state and is completely convertible into lifting of a mass in the surroundings." You should take note of two important aspects of this definition. First, work appears only at the boundary of the system and second; it appears only during a change in the state of the system. The SI unit of work is joule (J), which is the product of a unit force (one newton) acting through a unit distance (one meter); $1\text{J} = 1\text{N.m}$

Heat

Let us now understand what is heat? Heat is another type of energy in transit. Suppose we take two bodies at different temperatures (hot to different extent) and bring them in thermal contact with each other, what would we observe? Our common sense tells us that there would be transfer of energy from the hotter object to the cooler one. For example, if we add 100 cm^3 of water at 30°C to 100 cm^3 of water at 60°C taken in a beaker, mix the two and monitor the temperature of the mixture. We will find that the temperature of the mixture becomes about 45°C and starts decreasing gradually with time. The hot water has lost energy and the cold water has gained it hence the temperature becomes about 45°C . Further decrease is due to the loss of heat from the mixture to the surroundings (which are assumed to be at a lower temperature). Such an energy transfer that takes place because of a temperature difference is called heat flow or heat transfer, and energy so transferred is called **heat** and is symbolized as q . In terms of thermodynamics, we may define heat as,

"A form of energy that is exchanged at the boundary between a system and its surroundings by virtue of a difference in temperature between them and flows from a point of higher to a point of lower temperature and causes a change in the state of the system." You should take note of two important aspects of this definition. First, that the **heat appears only at the boundary** of the system and secondly, the **heat appears only during a change in the state of the system**.

Since heat is also a form of energy (in transit) so its SI unit is joule, J. Further, you should note that heat is an algebraic quantity having magnitude as well as sign. Heat is said to be positive when energy is transferred to a system from its surroundings (we say that heat is absorbed by the system). On the other hand,

heat is said to be negative when energy is transferred from a system to its surroundings (we say that heat is released or lost by the system).

Heat Capacity

Suppose we transfer a certain amount of heat, q to a system its temperature would increase by a certain value (ΔT) or for the temperature of the system to be increased by a certain value, ΔT we must supply a quantity of heat equal to q . The heat required is proportional to the change in temperature.

$$q = C(T_f - T_i) = C \Delta T \quad \dots(1.2)$$

The heat capacity C of an object is the proportionality constant between the heat q that the object absorbs or loses and the resulting temperature change ΔT of the object.

Where, T_f and T_i are the final and initial temperatures of the system. The proportionality constant, C is called **heat capacity**. Rearranging the equation, we get,

$$C = q / \Delta T \quad \dots(1.3)$$

For, $\Delta T = 1^\circ\text{C}$; $C = q$ $\dots(1.4)$

Thus, the **heat capacity** C , of a given system is defined as the amount of energy as heat needed to raise the temperature of the system by 1°C . Its units are energy per degree or energy per kelvin i.e., joule per kelvin, J K^{-1} or joule per degree Celsius, $\text{J }^\circ\text{C}^{-1}$.

It is observed that the quantity of heat required to raise the temperature of a given mass of the substance by a certain value depends on its nature. For example, 4 186 J of heat energy is required to raise the temperature of 1kg of water by 1°C , whereas to raise the temperature of 1kg of copper by 1°C we need only 387 J of heat.

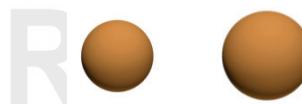
The word "capacity" here is somewhat misleading as it suggests that the system has some kind of a capacity of holding heat or has 'heat'.

You must note that 'heat' is not a material that is contained in an object or the object has a capacity to hold 'heat'. We can transfer any amount of heat to a system provided we have a body at temperature greater than the system.

Further, the transfer of heat to a system can be done under different conditions. If the transfer of heat is done under the conditions of constant volume, the associated heat capacity is called as **the heat capacity at constant volume**, C_V and if the transfer of heat is done under the conditions of constant pressure, the associated heat capacity is called as **the heat capacity at constant pressure**, C_p .

Let us take two balls of copper having different masses. These would require different amounts of heat to raise the temperature by a certain value say 1K. That is, these would have different heat capacities! This sounds ambiguous that two balls of same material have different heat capacities. In fact, it is due to the difference in their masses. It is therefore convenient to define a quantity like "heat capacity per unit mass" or **specific heat capacity**, c . The specific heat capacity would have the units of $\text{J K}^{-1}\text{g}^{-1}$ or $\text{J K}^{-1}\text{kg}^{-1}$ (depending on the units of mass). For one mole of a substance the corresponding heat capacities are known as molar heat capacity at constant volume, $C_{V,m}$ and molar heat capacity at constant pressure $C_{p,m}$ respectively. The units for molar heat capacities are $\text{J K}^{-1}\text{mol}^{-1}$. The specific heat capacity and molar heat capacity are intensive properties whereas heat capacity is an extensive property.

Let us take an example, to understand the difference between different types of heat capacities.



The heat capacities per unit mass are called **specific heat capacities** c_p and c_v

$$c_p = C_p / m$$

According to IUPAC, the adjective specific before the name of an extensive quantity is often used to mean *divided by mass* and if the symbol for the extensive quantity is a capital letter, the symbol used for the specific quantity is often the corresponding lower case letter.

Example 1.1: 20.70 kJ of heat was supplied to 5.0 mole of water at 25°C and the temperature of water increased to 80°C. Calculate the heat capacity of the water sample, molar heat capacity and specific heat capacity of water.

Solution: As per the Eq.(1.3) the heat capacity, C is defined as

$$C = q / \Delta T$$

We are given,

$$q = 20.70 \text{ kJ} \quad \text{and} \quad \Delta T = (T_f - T_i) = 80 - 25 = 55 \text{ }^{\circ}\text{C} = 55 \text{ K}$$

Substituting in the expression, we get, the heat capacity of the water sample,

$$C = \frac{20.70 \times 1000 \text{ J}}{55 \text{ K}} = 376.36 \text{ J K}^{-1}$$

The molar heat capacity can be obtained by dividing the value obtained above by 5.0, the number of moles of water in the sample.

$$\Rightarrow \text{Molar heat capacity, } C = \frac{376.36 \text{ J K}^{-1}}{5.00 \text{ mol}} = 75.27 \text{ J K}^{-1} \text{ mol}^{-1}$$

The specific heat capacity is the heat capacity per g; it can be obtained by dividing the molar heat capacity by the molar mass

$$\Rightarrow \text{Specific heat capacity, } c = \frac{75.27 \text{ J K}^{-1} \text{ mol}^{-1}}{18.00 \text{ g mol}^{-1}} = 4.181 \text{ J K}^{-1} \text{ g}^{-1}$$

The values of C_p and C_v for a given solid or liquid systems are not much different. However for gaseous systems the difference in their values is significant and for an ideal gas it is given by the following expression.

$$C_{p,m} - C_{V,m} = R \quad \dots(1.5)$$

Where, R is the gas constant. Further, the heat capacities depend on temperature implying that the amount of heat required to raise the temperature of a system by 1K is different at different temperatures. However, for small ranges of temperature, these do not change much and are usually taken as constant. We would talk more about the heat capacities and their temperature dependence in the Unit 3.

Solve the following question before moving ahead.

SAQ 5

0.5 mole of an ideal gas is taken in a container at 298 K. By what amount (give units also) would its heat capacity at constant pressure be more than its heat capacity at constant volume?

1.5 REVERSIBLE AND IRREVERSIBLE PROCESSES

The thermodynamic processes can be performed in two different ways i.e., ‘reversibly’ or ‘irreversibly’. The thermodynamic reversibility and irreversibility is different from the reversibility and irreversibility that you have learnt in the context of chemical reactions. In a reversible process the change in the state of the system is made to happen slowly in an infinite number of infinitesimal steps. On the other hand, the same change can be achieved irreversibly in one or a few steps.

Let us try to understand these terms with the help of an experiment. Let us take a thermodynamic system consisting of a certain amount of an ideal gas taken in a cylinder fitted with frictionless and massless piston having an area of cross section of $A \text{ m}^2$. A mass of 1 kg is placed on the piston and the whole system is placed in a thermostat at temperature T , Fig. 1.7 (a). The gas occupies a volume V_1 at an initial pressure equal to the atmospheric pressure and the pressure exerted by the mass on the piston; let's call this pressure p_1 . The thermodynamic state of the system would be given as (p_1, V_1, T) .

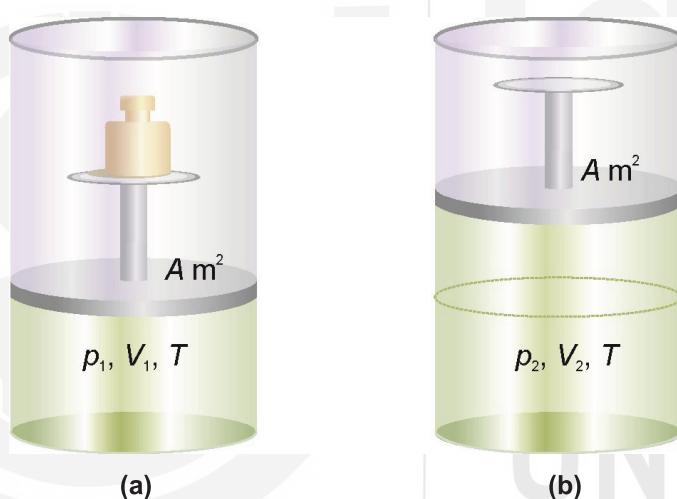


Fig. 1.7: Experimental design for understanding single step (irreversible) expansion of a gas.

Let's now remove the 1 kg mass from the piston; the pressure reduces to be equal to the atmospheric pressure; let's call it p_2 . The gas would expand to volume V_2 against the opposing pressure P_2 and produce a work w_1 . The new state of the system would be (p_2, V_2, T) Fig. 1.7 (b).

$$\text{Work} = w_1 = -p_2(V_2 - V_1) \quad \dots(1.6)$$

This work w_1 (done by the system) is generated in the surroundings. Let's move ahead and try to reverse the process by placing the 1 kg mass back on the piston. In this case the gas would undergo compression under the influence of the opposing pressure p_1 (1 atm + pressure due to 1 kg mass). The compression work would be

$$\text{Work} = w_2 = -p_{\text{op}}(V_1 - V_2) = -p_1(V_1 - V_2) \quad \dots(1.7)$$

You may note here that the amount of work (w_1) generated in the surroundings during the expansion process and work (w_2) that needs to be done by the

surroundings to bring the system back to initial state are not equal. Let us compute the work in the cyclic process; state 1 → state 2 → state 1.

$$\begin{aligned} w_{\text{cyclic}} &= w_1 + w_2 = -p_2(V_2 - V_1) - p_1(V_1 - V_2) \\ &= -p_2(V_2 - V_1) + p_1(V_2 - V_1) \\ w_{\text{cyclic}} &= (V_2 - V_1)(p_1 - p_2) \end{aligned} \quad \dots(1.8)$$

As the terms in both the brackets of Eq.(1.8) are positive therefore w_{cyclic} is positive. When we analyse the system and the surroundings we find that the system has come back to its original state but the surroundings have not. The expansion process generated some work in the surroundings but much more work was required to be done by the surroundings to get the system back to its original state. We say that some work has been destroyed in the surroundings in this cyclic process. Such a process is called an **irreversible process**.

Let us again take the thermodynamic system consisting of same amount of the ideal gas taken in a cylinder fitted with frictionless and massless piston having an area of cross section of Am^2 . Again a total mass of 1 kg is placed on the piston but in terms of 1000 masses of 1 g each, and the whole system as before is placed in a thermostat at temperature T , Fig. 1.8 (a). The gas would again occupy a volume V_1 at an initial pressure equal to the atmospheric pressure plus the pressure exerted by the 1 kg mass on the piston; i.e., p_1 .

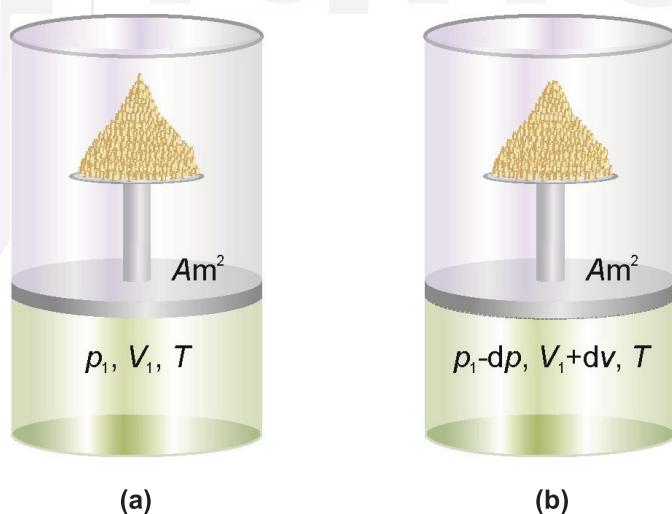


Fig. 1.8: Experimental design for understanding reversible expansion of a gas.

Now let's remove one of the 1 g masses from the piston. The pressure would decrease slightly (say by dp_1) and the gas would undergo slight expansion (by a volume dV_1) against the new pressure ($p_1 - dp_1$), Fig. 1.8 (b). This would generate a small amount of work (dw) in the surroundings.

We allow the system to attain equilibrium and remove another 1 g mass from the piston. Again the system expands a little and a work equal to dw_2 is obtained in the surroundings; again we let the system equilibrate. We continue the process of removing 1 g mass, allowing the system to equilibrate remove the next 1 g mass till all the 1 g masses are removed one by one. At the end of the process, i.e., when we remove the 1000th mass of 1 g, the system would reach state II (p_2, V_2, T); i.e., the gas expands from a volume V_1 to V_2 .

Now we try to perform the reverse process, i.e., we place a 1 g mass on the piston. The pressure would increase slightly and the gas would compress by a small volume. A work $+dw$ would be involved in this process. We allow the system to equilibrate and then put one 1 g mass on the piston. We repeat this process of placing 1g masses on the piston one by one; every time allowing the system to come to equilibrium. Once we place all the 1000 masses of 1g each on the piston we find that the system has come back to the state 1 (p_1, V_1, T).

It is found that the total work obtained from the system in the process of expansion ($V_1 \rightarrow V_2$) and the total work required to be done on the system during compression ($V_2 \rightarrow V_1$) are equal. In other words, no work is destroyed in the surroundings in the expansion-contraction cycle. Such processes are called thermodynamically reversible processes. If you think carefully you may note that the work done during the 2nd step of expansion process and the work obtained during the 999th step in the contraction process would be equal.

We have taken an example wherein the change from state-I (p_1, V_1, T) to state-II (p_2, V_2, T) was achieved in say 1000 small steps. Such an approach is a reasonably good approximation to reversible processes. *Ideally speaking for a process to be truly reversible, the change must be brought in an infinite number of infinitesimally small steps.* Which means it would need an infinite length of time to complete. Thus, we can say that the reversible processes are not real processes; these are ideal. We may approach the true reversible behaviour but not achieve it. In other words we can say that ***all real processes are irreversible.***

The process could be done in 10,000 steps using 100 mg mass each time or 100,000 steps using 10 mg mass each time and so on. To make it even better we could use 1 kg of sand and remove a grain of sand each time.

SAQ 6

Outline the differences between the thermodynamically reversible and irreversible processes.

1.6 THERMAL EQUILIBRIUM: THE ZEROTH LAW OF THERMODYNAMICS

Temperature is a familiar property (we all seem to know it), however it is quite difficult to define. We are also familiar with the fact that when a hot body and a cold body are brought into contact, the hot body becomes cooler and the cold body becomes warmer. The concept of temperature is based on the qualitative ideas of something being 'hot' or 'cold' as felt by us on the basis of our sense of touch. However, a measurement of temperature on the basis of sense of touch can be very vague as our senses may deceive us and the outcome may be unreliable. For example, if we stand bare feet with one foot on dry grass and the other on an adjacent marble floor in open on a hot sunny day; the floor would appear much hotter than the grass even though the two may be at the same temperature. Similarly, a steel spoon may appear warmer than the wooden table on which it is kept. The difference is due to the fact that our skin measures the rate of energy transfer (heat) from the object rather than its temperature.

Now, suppose you ask anybody ‘how can we measure temperature?’ The immediate answer would be ‘with the help of a thermometer’. In other words we all know that the thermometer as a device to measure temperature. Have you ever thought, what is the basis of this device? The principle of thermometer is based on two things: firstly, the concept of thermal equilibrium, and secondly, the fact that certain properties of materials depend on temperature. Let us first understand the meaning of thermal equilibrium. Let us bring two closed systems into a thermal contact with each other and observe the changes in the properties of both the systems. You may ask what are the systems and how do we observe changes?

For this, let us assume that we have got two identical cubes made up of a ‘novel’ material, which changes its colour with temperature. Let one of the cubes (system A) be ‘hot’ (red coloured) and the other (system B) be ‘cool’ (blue coloured) and we place these two in the two chambers (separated by an insulated partition) of an insulated box made up of a transparent material so that we can visually observe the colour changes taking place inside the insulated box (Fig. 1.9). Now when we remove the insulated partition what would we observe?

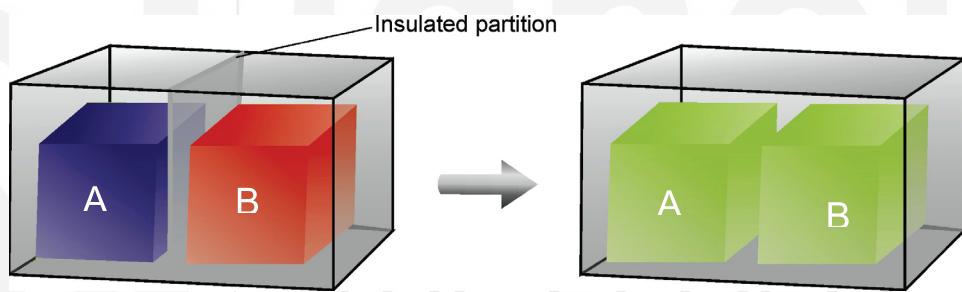


Fig. 1.9: A schematic diagram of a thought experiment (described in the text) designed to demonstrate the directionality of heat flow.

When two objects maintained at different temperatures are brought in thermal contact, they exchange heat with each other until they reach a state of thermal equilibrium and after that no further exchange of energy takes place between them.

The thermal equilibrium is characterized by the equality of a single parameter (temperature) was first stated by a Scottish chemist and physician, Joseph Black (1728–1799).

We would observe that the colors of the two cubes change gradually and eventually become the same indicating the attainment of equality of temperature—a state of equilibrium. Thereafter, there is no further change in colour as there is no further exchange of energy between the systems. Such an equilibrium that is a consequence of temperature being the same is called **thermal equilibrium**. The heat flows from higher temperature to lower temperature and continues till the two objects attain same temperature. Now if one of the objects happens to be a thermometer, the reading on the thermometer would change and become constant. This would indicate the temperature of the other object.

Let us extend our experiment and consider three systems, A, B, and C that are at different temperatures initially. The arrangement of the three systems is given in Fig. (1.10). In this arrangement we have separated system A and B by an insulating wall and have introduced thermally conducting slabs in such a way that these provide thermal contact between system A and system C and also between system B and system C. Thus, in our experiment system C can interact thermally with system A and B whereas system A and B cannot interact with each other.

Having set the experiment we observe the three systems from outside. Remember, our insulating box is made up of a transparent material that permits us to observe the systems inside. What would we observe?

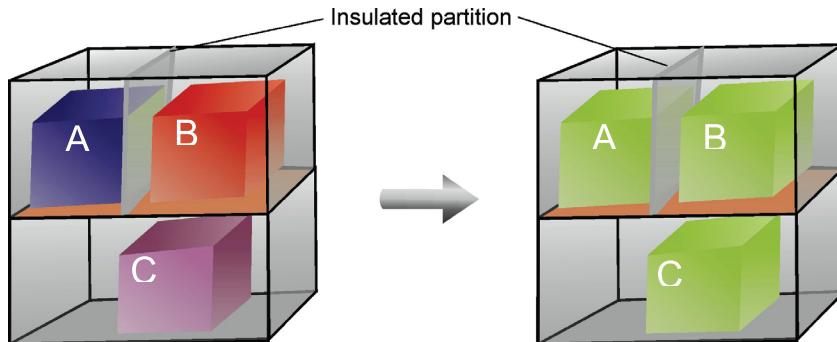


Fig. 1.10: A schematic diagram of a thought experiment (described in the text) to demonstrate the Zeroth law of thermodynamics.

We would observe that the colors of the three cubes representing the three systems change with time. After sufficient amount of time is passed the three systems, would be found to have same colour indicative of same temperature. Since there was a thermal contact between system A and system C we expect them to be at thermal equilibrium. Similarly, the thermal contact between system B and system C also allows for a thermal equilibrium to be achieved between them. The question comes up is that how do we explain the thermal equilibrium between system A and system B as we did not allow any thermal interaction between the two?

The Zeroth Law is identical in form to a famous logical argument using deductive reasoning viz., if $\alpha = \beta$ (first premise), and $\beta = \gamma$ (second premise), then $\alpha = \gamma$ (conclusion). Herein we arrive at a conclusion based on two propositions. In mathematical terms, the Zeroth law of thermodynamics is said to be **transitive**.

This observation, in fact, is the essence of the Zeroth law of thermodynamics which can be stated as, “*If two thermodynamic systems, A and B are in thermal equilibrium with a third thermodynamic system, C then the two thermodynamic systems (A and B) are also in thermal equilibrium with each other*”. The importance of this law was recognized only after the other laws of thermodynamics were formulated and is fundamental to them, therefore is called the Zeroth law.

1.7 SUMMARY

In this unit we began by defining energetics as the study of energy in terms of its flow and transformation within a system or between a system and its surroundings. We highlighted its wide applicability and stated that in this course we are going to focus our attention on the flow and transformation of energy within chemical systems or between the chemical systems and their surroundings.

This was followed by introducing thermodynamics as a domain of science based on laws formulated by extensive observations of the macroscopic world. We defined thermodynamics as a branch of science that deals with the relationship between heat and other forms of energy and discussed the importance of thermodynamics in studying chemical reactions. Thereafter we took up the terms, like system, its types, state of system; the thermodynamic

properties etc., commonly used in the study of this important scientific domain and explained them with the help of suitable examples. This was followed by a brief discussion on thermodynamic processes; any change in state of a given system is termed as a thermodynamic process.

Having defined the terms used in thermodynamics, we revisited the concepts of heat, work and heat capacity etc. and explained the sign convention for heat and work to be used in the context of thermodynamics. This was followed by a discussion on important concepts of thermodynamic reversibility and irreversibility. A thermodynamically reversible process is a process, which is accomplished, in an infinite number of infinitesimally small steps.

Thereafter we introduced the concept of thermal equilibrium and used the same to explain the way a thermometer works. The argument was extended to introduce the Zeroth law of thermodynamics whose significance was outlined.

1.8 TERMINAL QUESTIONS

1. What is energetics?
2. A 10 g spherical ball of copper was heated by passing electrical current. If a transfer 100 J of energy increased the temperature of the sphere by 22°C . Calculate the specific heat capacity of copper. Assume that no heat was lost during the heating process.
3. Define and differentiate between intensive and extensive variables giving examples.
4. Calculate the amount of heat required to increase the temperature of 1.00 mole of argon from a temperature of 100 K to 900 K in:
 - a) an isobaric process and
 - b) in a isochoric process.(Given: $C_{V,m} = 12.47 \text{ J K}^{-1}\text{mol}^{-1}$ and $C_{p,m} = 20.78 \text{ J K}^{-1}\text{mol}^{-1}$)
5. What is meant by thermodynamic reversibility?
6. State Zeroth law of thermodynamics.

1.9 ANSWERS

Self-Assessment Questions

1. In the context of Chemical reactions, the thermodynamics
 - Provides a criterion for determining the feasibility of a reaction
 - Provides the criteria and conditions for the equilibrium state for a spontaneous process
 - Helps in predicting the direction of the system to attain equilibrium
 - Can provide information about the extent of reaction in an equilibrium reaction

2. A thermodynamic system that allows the exchange of energy as well as matter with the surroundings is called an open system, for example, food being cooked in an open vessel. On the other hand if the system permits the exchange of energy but not the matter it is termed as closed, e.g., cooked food kept in a closed metallic container. The isolated system does not permit the exchange of either the energy or the matter. The food in an insulated closed container is an example of an isolated system.
3. The given properties can be categorized as follows:

Extensive properties	Intensive properties
Area	Density
Volume	Temperature
Energy	Dielectric Constant
Pressure	Refractive index

4. a) The state of a system refers to its current condition identified in terms of its characteristic physical properties. If the thermodynamic properties characterising the system are defined the state is said to be defined. The pressure, p ; volume, V ; temperature, T ; and density, ρ , are examples of some of the thermodynamic properties of a system.
- b) No, a cyclic process cannot be a one step process. The requirement of the cyclic process is that the system must be back to its initial state, however, in a single step process the state of the system gets changed.
5. We know that for one mole of an ideal gas $C_{P,m} - C_{V,m} = R$ or in general, $C_P - C_V = nR$.

Substituting the values $C_P - C_V = 0.5 \text{ mol} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

$$= 4.157 \text{ J K}^{-1} \text{ mol}^{-1}$$

Therefore, the heat capacity for the given system at constant pressure will be 4.157 J K^{-1} more than the heat capacity at constant volume.

6. The following are the differences between the thermodynamically reversible and irreversible processes.
- In a reversible process, the thermodynamic system undergoes a change in state through a specified sequence of infinite number of infinitesimal steps each giving a new state whereas the irreversible process occurs in one or a few number of steps.
 - In case of reversible process, the system and the surroundings acquire equilibrium at every step whereas in irreversible process such an equilibrium does not exist

- In case of reversible process, the change in state is reversed through the same sequence of states in the reverse order whereas in irreversible process the same sequence in the reverse order is not observed

Terminal Questions

- 'Energetics' refers to the study of energy in terms of its flow and transformation within a system or between a system and its surroundings. The energy could be in the form of heat, light, radiation or mass etc.
- The specific heat capacity is defined as the quantity of energy as heat required to raise the temperature of 1 g of a substance through 1°C . Mathematically

$$c = \frac{q}{m\Delta T}$$

we are given $q = 85 \text{ J}$; $m = 10 \text{ g}$ and $\Delta T = 22^{\circ}\text{C}$.

Substituting the values, we get

$$c = \frac{85 \text{ J}}{10 \text{ g} \times 22 \text{ K}} = 0.386 \text{ JK}^{-1}\text{g}^{-1}$$

- The thermodynamic properties whose values do not depend on the amount of the substance are called intensive properties and the ones, which are dependent on the amount, are called extensive properties. For example, the mass and volume of a substance would depend on its amount. A sample of water having 1.00 moles of it will weigh 18 g and would occupy a volume of 18 cm^3 (at room temperature; assuming ρ to be 1.0 g cm^{-3}) whereas 5.00 moles of water would have five times the mass and the volume. On the other hand density is an intensive property, as any two samples of a substance (if they are from the same source) would have same density.
- a) We know that for isobaric process (occurring at constant pressure), the heat required to raise the temperature is, $q_p = nC_{p,m}\Delta T$

Given: $C_{p,m} = 20.78 \text{ J K}^{-1}\text{mol}^{-1}$, $n = 1.00 \text{ mol}$,
 $\Delta T = 900 - 100 = 800 \text{ K}$

Substituting in the expression,

$$q_p = 1.00 \text{ mol} \times 20.78 \text{ JK}^{-1}\text{mol}^{-1} \times 800 \text{ K} = 16624 \text{ J} \Rightarrow 16.624 \text{ kJ}$$

- Similarly, for isochoric process (occurring at constant volume), the heat required to raise the temperature is, $q_v = nC_{v,m}\Delta T$

Given: $C_{v,m} = 12.47 \text{ J K}^{-1}\text{mol}^{-1}$, $n = 1.00 \text{ mole}$,
 $\Delta T = 900 - 100 = 800 \text{ K}$

Substituting in the expression,

$$q_v = 1.00 \text{ mol} \times 12.47 \text{ J K}^{-1}\text{mol}^{-1} \times 800 \text{ K} = 9976 \text{ J} \Rightarrow 9.976 \text{ kJ}$$

5. In thermodynamics a process implies a change in state of a system. Thermodynamic reversibility concerns the nature of process i.e., the way a process occurs. A reversible process is that process which takes place in infinite number of infinitesimally small steps. At each step there is an equilibrium between the system and the surroundings and on reversing the order of the steps the initial state can be regained.
6. The Zeroth law of thermodynamics states that “If two thermodynamic systems, A and B are in thermal equilibrium with a third thermodynamic system, C then the two thermodynamic systems (A and B) are also in thermal equilibrium with each other”.

